

Silicon oxide formation for TFTs using humid ozone-enriched gas ambient at low temperature

P. N. Hai^{1,2}, S. Nishio¹ and S. Horita¹

¹Japan Advanced Institute of Science and Technology (JAIST)

1-1, Asahidai, Tatsunokuchi, Ishikawa 923-1292 Japan

Tel: (+81)-0761-51-1561, Fax: (+81)-0761-51-1149, e-mail: pnhai@jaist.ac.jp

²Faculty of Physics, Hanoi University of Science, 334 Nguyen Trai, Hanoi, Vietnam

Abstract

Humid ozone-enriched ambient, created by bubbling (O_3+O_2) gas in H_2O or H_2O_2 , enhanced the silicon oxide growth on the Si substrate at 250°C. The film thickness was controllable with the high growth rate of 1.4 Å/min. The XPS data show that the oxide layer on Si(111) has the same transition layer structure as the thermal SiO_2 film. By combination with the short-time treatment at higher temperature (below 500°C), the electrical characteristics of SiO_2 thin films were improved. The operation of polycrystalline Si thin film transistors using this oxide film indicates that the new growth method is applicable for low-temperature device fabrications.

1. Introduction

Polycrystalline Si thin film transistors (poly-Si TFTs) processed at low temperature on low-melting-temperature substrates have received a great attention in display-device technologies. To realize the possible TFT applications, the formation of device-quality SiO_2 gate oxide film and SiO_2/Si interface, as well as the ability to control the grown film thickness at below 500°C are strongly required [1]. Currently, plasma-enhanced chemical vapor deposition (PE-CVD) and related means are employed in formation of silicon oxide thin films at low-temperature process [2]. However, energetic particles like ions introduce serious damage to the interface and the oxide film, leading to further extensive treatments to minimize this problem. To pursue the simplified and low-cost fabrication of device-quality SiO_2 gate layers, other alternative approaches need to be investigated.

The utilization of dry ozone-enriched ambient is shown to create a relatively large enhancement in thermal oxidation of silicon at low temperature, because of plasma damage free and the formation of the SiO_2/Si interface not on but beneath the Si surface [3]. In order to enhance more the growth rate of dry ozone-enriched oxidation, some researchers have used high ozone concentration gas [4] and ultra-violet light irradiation to ozone-enriched gas [5]. However, after oxidizing in 180 min, the film thickness is less than 6 nm and slowly saturated at 400°C [3,4], while it is just about 15 nm at 500°C [3]. This seems difficult to apply for productions of poly-Si TFTs, which require the thicker gate oxide film in low-thermal budget process. In this paper, we

propose a new and simple ozone-enriched growth method, in which the dry gas mixture of (O_2+O_3) is humidified by bubbling in pure de-ionized (DI) H_2O or in H_2O_2 before flowing into the heated furnace (hereafter named as wet ozone-enriched growth, WO_3-H_2O or $WO_3-H_2O_2$, respectively). The chemical bonding configurations and the electrical characteristics of SiO_2 thin films on n-type Si(111) substrates prepared by this new procedure are reported and discussed to reveal the adaptability of the WO_3 oxide films in poly-Si TFT application.

2. Experiments

The ozone-enriched gas (0.8% concentration) was produced by a conventional discharge-type ozone generator using pure oxygen gas with the flow rate of 0.7 l/min. The mixture gas was then bubbled in pure DI water or H_2O_2 (30% concentration) prior to flowing into the quartz tube in a controlled furnace through the Teflon pipe. After standard RCA cleaning, n-type (111)-oriented Si substrates, having the resistivity of 10 Ω cm, were placed in the reaction quartz tube. The treatment temperature was kept at 250°C for periods up to 180 min in order to investigate the growth rate of the WO_3 growth. Reference samples of the same Si substrate were formed by the dry ozone (0.8%) oxidation at 480°C in 60 and 180 min.

After the post-growth annealing in N_2 gas in 30 min at 350°C, MOS capacitors were fabricated by forming the Al-gate electrode (with the diameter of 0.1 or 0.2 mm) on SiO_2 thin films, then subjected to the post metallization annealing in N_2 gas in 30 min at 350°C. The electrical properties of grown SiO_2 thin films were clarified by current density-electric field (J-E) measurements in MOS capacitors. The chemical compositions of the oxide films as well as the nature of the suboxide species lying near the SiO_2/Si interface were determined by using X-ray photoelectron spectroscopy (XPS Surface Science Instruments S-PROBE). A very thin thermal SiO_2 layer on Si(111) was also prepared by dry oxygen oxidation at 900°C as the XPS reference sample. Fourier transform infrared (FT-IR) measurements, by JASCO FT-IR 670 spectroscopy with a resolution of 4 cm^{-1} , were employed to characterize chemical bonding configurations incorporated in the oxide thin films. The equivalent oxide thickness was determined by ellipsometry ULVAC

ESM-1 system, or from the XPS measurements [6] if needed.

3. Results and discussion

The dependence of the equivalent oxide thickness of SiO₂ thin films produced by WO₃-H₂O and WO₃-H₂O₂ methods at 250°C, measured by the ellipsometry, on the exposure time was depicted in Fig. 1. The film thickness increases with the exposure time and seems not to be saturated in both cases. The oxide growth rate in WO₃-H₂O₂ was higher than that in WO₃-H₂O, and they are much thicker than the growth rate in dry ozone oxidation at 480°C. The average growth rate of SiO₂ films was about 1.2 and 1.4 Å/min at 250°C by WO₃-H₂O and WO₃-H₂O₂ growth, respectively, and reached to the higher value (~2.5 Å/min) in the first 30-min exposure. These values are bigger than the reported data, which were deduced from the dry ozone oxidation at higher temperature and using the higher ozone concentration [4].

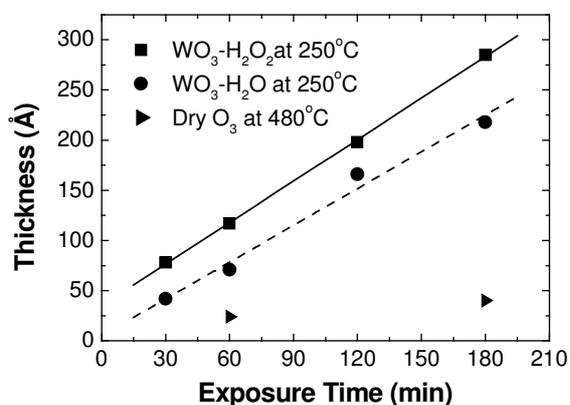


Fig. 1: Thickness dependence of SiO₂ thin films, grown at 250°C by WO₃-H₂O and WO₃-H₂O₂ methods and at 480°C by dry O₃ oxidation, on exposure time.

Figures 2(a) and 2(b) show the XPS spectra in the Si 2p region for the reference thermal SiO₂/Si (with the oxide thickness of 3.2 nm) and a 3.0-nm SiO₂ layer on Si grown by WO₃-H₂O method at 250°C. The mentioned oxide film thickness was deduced from the analysis of the XPS spectra [6]. In both cases, the doublet peaks around the binding energy of 99 eV are due to Si 2p_{3/2} and 2p_{1/2} levels of the Si substrate, while the broader one around 104 eV is due to the SiO₂ layer. The signatures of the suboxide species Siⁿ⁺ (n≤3) and Si-H bonding in each oxide film, revealed from the deconvolution of the above XPS spectra by least-square curve fittings, are also shown in Figs. 2 (a) and 2(b). The normalized ratios ($J_{Si^{n+}}\delta/J_{Si}$) - in which $J_{Si^{n+}}$, J_{Si} and δ are the XPS intensity per unit length of each suboxide state, the intensity per unit length of the Si substrate and the suboxide layer thickness (as illustrated in Fig. 3), respectively - were then calculated for both oxide films and depicted in Fig. 4. In this calculation, we assumed that the suboxide layer thickness δ is much smaller than the mean free path of photoelectrons in SiO₂ and Si, and that the suboxide layer is localized at the SiO₂/Si

interface. The ratio for the Si²⁺ suboxide is much lower than those of the other suboxide states. This is a typical result for Si(111) as reported previously [6]. Within the experimental error, it seems that the densities of the suboxide states in the thermal SiO₂ layer are comparable to those in the SiO₂ layer formed at 250°C by WO₃-H₂O growth. This fact also means that the WO₃ oxide layer on Si(111) has the same transition layer structure as the thermal SiO₂ film.

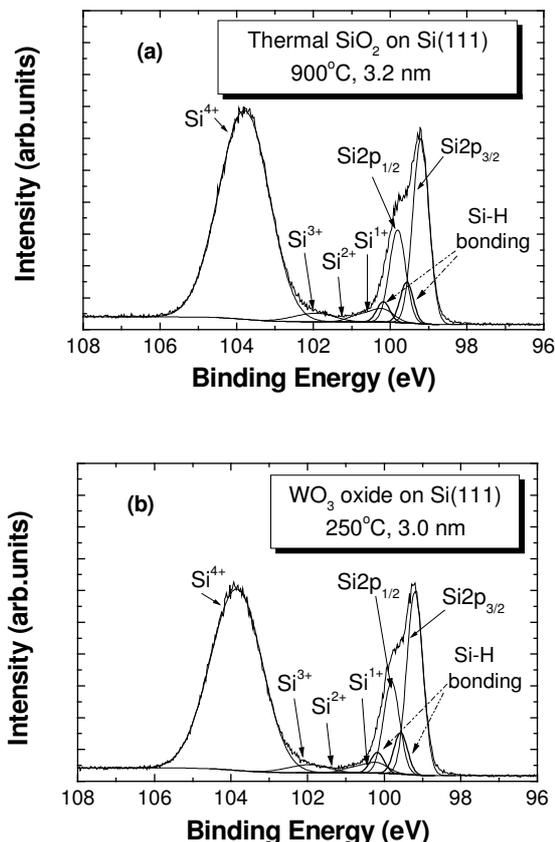


Fig. 2: XPS spectra measured on 3.2-nm thermal oxide (a) and 3.0-nm WO₃-H₂O oxide layer (b) on Si(111).

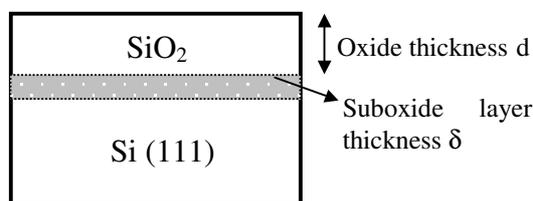


Fig. 3: Layer structure of a WO₃ oxide film on Si(111).

The measured FI-IR spectra in the oxide films prepared by WO₃-H₂O and WO₃-H₂O₂ growth in about 180 min were similar as illustrated in Fig. 5. The weak and broad asymmetric absorption band centered at 3500 cm⁻¹ is the overlapping signals of absorbed water and Si-OH bonding groups [7]. The strong vibration frequency at 1065 cm⁻¹ and the weaker one at about 800 cm⁻¹ are well-known attributed to the stretching and bending modes of the O atoms in the Si-O bonds, respectively

[2,7,8]. The absorption frequency of Si-O stretching mode in WO_3 oxide films is lower than that of 1075 cm^{-1} in the thermal oxide. In addition, the vibration band at about 930 cm^{-1} is associated to the stretching mode of Si-OH bonds [2,7,8].

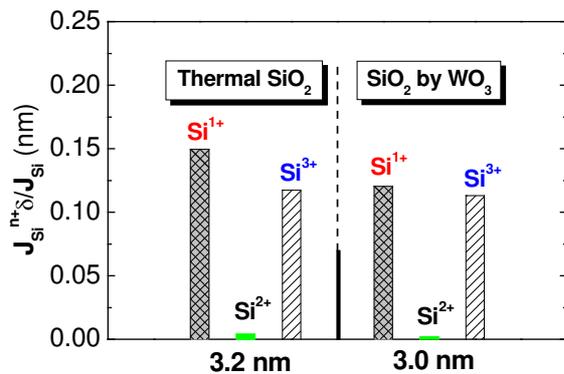


Fig. 4: Normalized ratios $J_{\text{Si}}^{n+}/J_{\text{Si}}$ (see text for details) of suboxide species in the 3.2-nm thermal oxide layer and the 3.0-nm WO_3 oxide layer on Si(111).

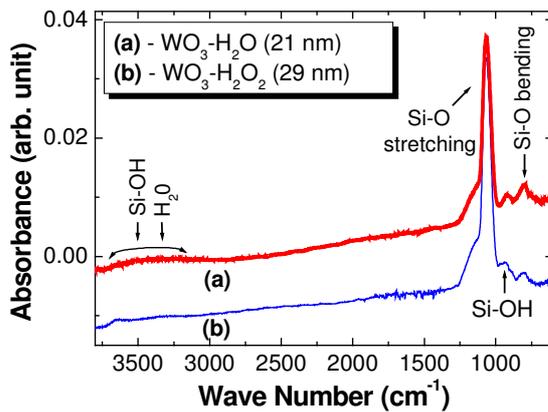


Fig. 5: FT-IR spectra observed in the SiO_2 thin films formed at 250°C by $\text{WO}_3\text{-H}_2\text{O}$ (a) and $\text{WO}_3\text{-H}_2\text{O}_2$ (b) growth.

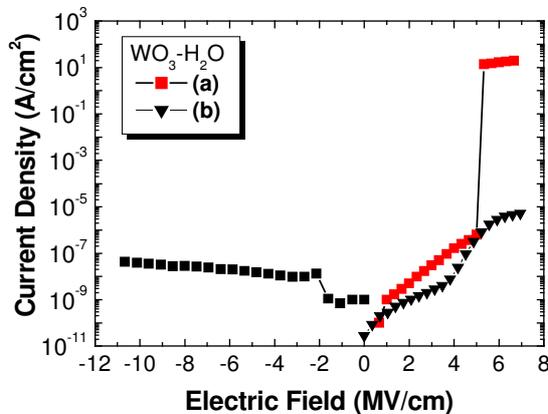


Fig. 6: J - E characteristics observed in the n -type Si(111) substrates prepared by $\text{WO}_3\text{-H}_2\text{O}$ method at 250°C in 90 min (a); at 400°C in 30 min and then at 250°C in 90 min (b).

Figure 6(a) shows typical J - E characteristics of the SiO_2/Si structure prepared by 90-min $\text{WO}_3\text{-H}_2\text{O}$ growth at 250°C . The same features were monitored in $\text{WO}_3\text{-H}_2\text{O}_2$ oxide films under the same experimental condition. Much lower breakdown field in the positive region was monitored in a 90-min growth sample as compared with the negative one. The gate oxide integrity measurement revealed that only 48% of MOS capacitors (among 30 ones prepared by $\text{WO}_3\text{-H}_2\text{O}$ method at 250°C in 90 min) withstand the breakdown field between 5 to 6.5 MV/cm. This rather low breakdown frequency may be due to the roughness near the interface and relatively high structural defects, which were possibly formed by incomplete reaction between Si and reactant species at low temperature of 250°C . The OH bonding groups in WO_3 films, revealed by FT-IR measurements, are likely among the ones accounted for oxide structural defects, because Si-OH bond forms electron traps in the oxide film. Further study to find an efficient way to remove the OH groups from WO_3 oxide films is important. However, at this stage, short treatment at higher temperature in the beginning of the growth process may help to improve the breakdown frequency at the higher electric field. A new approach was proposed: the Si substrates are first oxidized in $\text{WO}_3\text{-H}_2\text{O}$ (H_2O_2) ambient in 30 min at higher temperature between 350 to 500°C (to establish a better interface SiO_2/Si and to minimize the electrical defects at maximum temperature of 500°C as required), then followed by normal $\text{WO}_3\text{-H}_2\text{O}$ (H_2O_2) at 250°C in 90 min (to advance the high growth rate at this temperature). Fig. 7 illustrates the breakdown frequency statistics of $\text{WO}_3\text{-H}_2\text{O}$ grown SiO_2 thin films ($d \sim 10 \text{ nm}$) pre-oxidized at temperature of 250, 350, 400 and 500°C . The enhancement of the breakdown field was clearly monitored: 65% of MOS capacitors can work at the higher electric field between 5 to 8 MV/cm for the thin films pre-treated at temperature of 350°C and 400°C , and 87.5% of those at 500°C . The leakage current in the positive electric field in these films was also improved as shown in Fig. 6(b), in which the oxide film was formed by $\text{WO}_3\text{-H}_2\text{O}$ firstly at 400°C in 30 min and then followed at 250°C in 90 min. The similar trend was observed in the case of $\text{WO}_3\text{-H}_2\text{O}_2$ treatment. From the above results, it can be concluded that the oxide film formed by combination of wet ozone growth at 500°C and 250°C has relatively good electrical properties. Therefore, it is necessary to investigate a device operation, for example poly-Si TFTs, using WO_3 gate oxide layer.

Figure 8 shows the schematic cross section view of the fabricated TFT on the Pyrex glass substrate. A 80-nm-thick amorphous Si film was deposited on a Pyrex glass substrate at 350°C in ultra high vacuum chamber. The Si film was then crystallized by Nd:YAG pulse laser annealing (wavelength: 532 nm; pulse width: about 6-7 ns; the laser fluence: $150 \text{ mJ}/\text{cm}^2$; the pulse number: 10) at the substrate temperature of 250°C [9]. After that, phosphorous ions with the accelerate voltage of 30 keV and a dose of $3 \times 10^{15} \text{ cm}^{-2}$ were implanted into the poly-Si film to form the source and drain regions. The activation of the implanted impurity was also carried out by Nd:YAG pulse laser annealing. The beam was scanned over the sample. The gate oxide film was then

created by the above-mentioned $\text{WO}_3\text{-H}_2\text{O}$ process at 500°C and 250°C . The electrodes were formed by vacuum evaporation of Al. Finally, post metallization annealing was carried out in order to obtain the Ohmic contacts. The highest temperature of this process was 500°C .

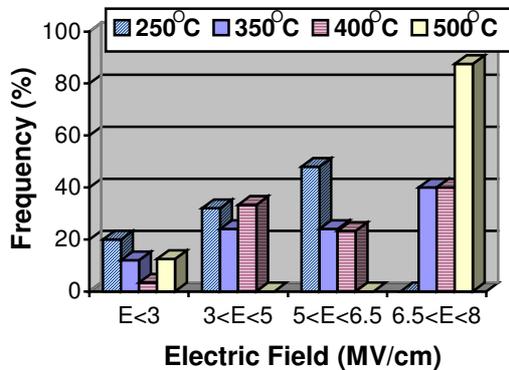


Fig. 7: Breakdown frequency statistics of 30 MOS capacitors pre-oxidized at 250, 350, 400 and 500°C by $\text{WO}_3\text{-H}_2\text{O}$ method.

Figure 9 shows drain current-gate voltage ($I_D\text{-}V_G$) and gate current-gate voltage ($I_G\text{-}V_G$) characteristics of the fabricated poly-Si TFT when the channel length and width are $10.5\mu\text{m}$ and $6.5\mu\text{m}$, respectively.

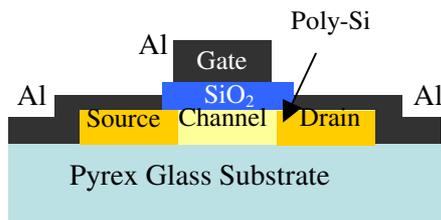


Fig. 8: Cross section view of poly-Si TFT.

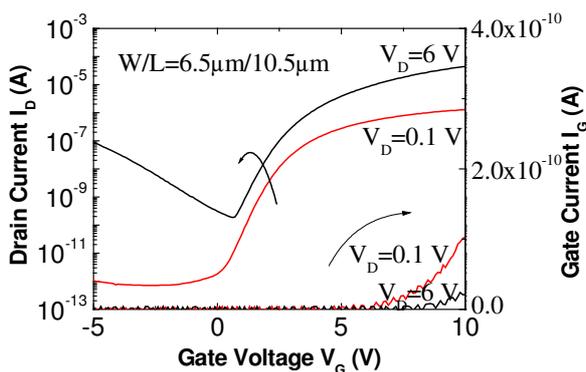


Fig. 9: Typical $I_D\text{-}V_G$ characteristics of a poly-Si TFT.

It is obvious that the drain current is controlled under the gate voltage, which means this TFT is operated. The gate current is less than 1×10^{-10} A, which is negligible to I_D . The field-effect mobility was estimated about $16.2 \text{ cm}^2/\text{Vs}$ from the $I_D\text{-}V_G$ characteristics at $V_D=0.1 \text{ V}$. The field-effect mobility of the fabricated device is rather low as compared to the reportedly standard data (about $300 \text{ cm}^2/\text{Vs}$). Several probable reasons can be accounted for this problem: the grain boundary location and the grain

size were not well controlled; the fabrication technology was not optimized. If the fabrication technique is improved, we could then obtain the better transfer property. However, the obtained results clearly indicate that the oxide film formed at low temperature by wet ozone growth is possible for poly-Si TFTs.

4. Conclusion

Simple but effective WO_3 growth method results in the relatively high SiO_2 growth rate of $1.4 \text{ \AA}/\text{min}$ at 250°C . The film thickness is also controllable without saturation. By combination with the short-time treatment at higher temperature (below 500°C) in the same ambient, the electrical characteristics of the SiO_2 thin films were improved. Poly-Si TFTs with the WO_3 gate oxide layers were fabricated at maximum temperature of 500°C . Poly-Si TFTs showed transistor operation, having the field-effect mobility of $16.2 \text{ cm}^2/\text{Vs}$. Therefore, the proposed oxide growth method is promising for device fabrication of at low temperature. Further optimization of the growth process at lower temperature for the better electrical properties of SiO_2 films is under way.

Acknowledgments

The authors thank Mr. M. Seki, who graduated from JAIST, for assistance in TFT fabrication.

Reference

1. T. Sameshima, J. Non-Cryst. Solids 227-230 (1998) 1196.
2. S. B. Bang, T. H. Chung and Y. Kim, Thin Solid Films 444 (2003) 125.
3. A. Kazor and I.W. Boyd, Appl. Phys. Lett. 63 (1993) 2517.
4. K. Koike, G. Inoue, S. Ichimura, K. Nakamura, A. Kurokawa and H. Nonaka, Mater. Res. Soc. Symp. Proc. 567 (1999) 121.
5. T. Nishiguchi, Y. Morikawa, M. Miyamoto, H. Nonaka and S. Ichimura, Ext. Abstr. (62nd Autumn Meet. 2001), Japan Society of Applied Physics, 13a-W-1.
6. P. G. Grunthaner, M. H. Hecht, F. J. Grunthaner and N. M. Johnson, J. Appl. Phys. 61 (1987) 629
7. K. Sano, S. Hayashi, S. Wickramanayaka and Y. Hatanaka, Thin Solid Films 281-281 (1996) 397.
8. A. Barranco, F. Yubero, J. Cotrino, J. P. Espinós, J. Benítez, T. C. Rojas, J. Allain, T. Girardeau, J. P. Rivière and A. R. González-Elipe, Thin Solid Films 396 (2001) 9.
9. S. Horita, Y. Nakata and A. Shimoyama, Appl. Phys. Lett. 78 (2001) 2250.